Process for Complex Transient Liquid Phase Sintering of Powder Metal

This invention relates to a process for the compaction and sintering of powder metal. More particularly, this invention relates to a process for the compaction and sintering of powder metal employing complex transient liquid phase sintering.

As is known, low cost water atomized or atmospherically or carbon reduced iron and steel powders are commonly pressed and sintered to produce powder metal parts. In the "as sintered condition", such parts have a density in the range of from 80 to 95 % of theoretical density unless subsequent densification steps are performed or costly methods of consolidation are used. High density is important in a powder metal part because mechanical properties improve as the density (or reduction in the amount of porosity) increases. Tensile strength is almost a linear function of density. Ductility, toughness and fatigue strength are dependent on high density and increase significantly at low levels of porosity.

Commonly used methods to achieve high densification are double pressing and double sintering, warm compaction, high velocity compaction, hot isostatic pressing, pneumatic isostatic forging and powder forging, among others.

The prevalent method for producing low alloy steel powder metal parts involves the blending of either iron powder, co-diffused or low alloy steel powders or combinations thereof so that the sintered part contains such elements as nickel, chromium, molybdenum, copper, graphite and/or other alloying elements. Such powders are blended with lubricants to form a homogeneous mixture. The most commonly used lubricants are EBS (Ethylene Biostearamide), lithium stearate and zinc stearate. Such lubricants remain in solid form during the pressing operation.

One known technique of producing a powder metal part involves the steps of mixing a powder metal mass with graphite and a lubricant, such as a PS1000 b lubricant supplied by APEX Advanced Materials, LLC, of Cleveland, Ohio, to form a generally homogeneous mixture and of thereafter pressing and sintering the mixture into a sintered product using a single press and sinter process. This technique results in an intermediate to high dense product in the upper end of the 80 to 95 % of theoretical density range.

It is an object of the invention to be able to obtain a powder metal part that has 99+% of theoretical density.

It is another object of the invention to provide a process that uses a single pressing step and single sintering step to achieve a powder metal part that has 99+% of theoretical density.

It is another object of the invention to provide an economical method of producing powder metal parts that achieve a higher density than prior art techniques.

It is another object of the invention to provide a sintered metal powder product with a uniform density of 99+% of theoretical density throughout the product.

Briefly, the invention provides a process in which a metal powder is mixed with a lubricant and at least one liquid phase former to form a mixture, compressed and then sintered into a dense product with a density of 99+% of theoretical.

The lubricant that is used has a characteristic of transforming from a solid to a viscous liquid at low pressure and temperature and functions, in accordance with the invention, to distribute the liquid phase former over the particles of the metal powder. Such a lubricant is the above APEX PS1000 b lubricant that transforms from a solid to a

viscous liquid when pressed in a compact at about 4 TSI at room temperature. Other suitable lubricants of this nature are lauric acid and Johnson's Floor Wax of the S.C. Johnson Company,

The liquid phase former that is used has a characteristic of forming a liquid phase during sintering and of becoming part of the final product after sintering. For example, the liquid phase former is at least one of synthetic graphite, nickel, boron, phosphorous and compounds of boron and phosphorous. Other liquid phase formers are aluminum, copper, molybdenum, nickel, silicon, sulfur, zinc and their alloys. Further, the liquid phase former such as nickel, boron and phosphorous and compounds thereof should be finer than 20 microns and, preferably, finer than 10 microns whereas the synthetic graphite is finer than 10 microns and, preferably, finer than 2 microns.

Compressing of the mixture is accomplished by means of uniaxial, cold isostatic or other consolidation methods at a pressure sufficient to liquefy and uniformly distribute the lubricant within the compressed mixture with the lubricant effecting a uniform distribution of the liquid phase former on the particles of the metal powder.

In addition, during compression of the mixture, the liquefied lubricant forms a liquid film between the mixture and the tool in which the mixture is being compacted to eliminate friction forces between the mixture and the tool so that a green compact with a uniform density throughout the compact is obtained.

Sintering of the compressed mixture, i.e. green compact, occurs at a sintering temperature sufficient to evaporate and drive off the lubricant and to effect a liquid phase sintering of the liquid phase former with the particles of the metal powder to obtain a compressed and sintered product having a density of 99+% of theoretical density. During the thermal cycle of sintering, under a controlled atmospheric

environment the surface composition will form a low melting phase. This system provides for rapid transport or slippage of solid particles and therefore, rapid sintering and densification.

The process is particularly economic in obtaining ferrous or non-ferrous parts through a single pressing and sintering by coating the particles with a material that has a liquid phase forming component and that has high solubility of the solid phases.

These and other objects and advantages will become more apparent from the following detailed description.

The invention provides a method of producing ferrous or non-ferrous powder metal parts which can be single pressed by conventional uniaxial (movement of a pressing tool in a single direction) or cold isostatic methods and sintered to full density without the need for further compaction or densification steps.

As an example, a metal powder of elemental minus 100 (-100) mesh iron or low alloy steel is mixed with a lubricant that has a characteristic of transforming from a solid to a liquid under low pressure and temperature, e.g. 4TSI at room temperature, and of evaporating under a sintering temperature, for example APEX PS 1000 b, lauric Acid or Johnson's Floor Wax of S.C. Johnson Company, and a liquid phase former, such as extra fine synthetic graphite grade Timcal KS6, made by Timcal Ltd., of Bodio, Switzerland or less than 10 micron size graphite made by Asbury Carbon, Inc. of Asbury, New Jersey that has a characteristic of forming a liquid phase during sintering and of becoming part of the final product after sintering.

The resultant mixture is then compacted at a pressure of in the range of from 30 to 70 tons per square inch or through use of high velocity compaction in a uniaxial or high compaction press and sintered at an appropriate temperature in the range of from

2070 to 2500 degrees F, in hydrogen and hydrogen based atmospheres, or nitrogen in an all graphite furnace or vacuum with a preferred temperature of from 2300 to 2500 degrees F. from 10 to 60 minutes at temperature to permit the metallic particles to densify to 99+% of theoretical density in the final product.

The first required step is to distribute the liquid phase former uniformly around the solid phase particle, i.e. a metal powder particle, and to cause the liquid phase former to coat and bond to the metal powder particle with a high degree of uniformity on the majority of the powder metal particles. During the thermal sintering cycle, the surface and surface composition of the metal particle and the liquid phase former form a surface composition that upon further heating will liquefy forming a liquid film and provides surface tension which aids the densification process.

Thus, in accordance with the invention, the powder mixture of solid particle(s) of pure metal(s) or alloy(s) or co-diffused materials is blended with a lubricant (formulation) and one or more liquid phase former(s). The liquid phase formers generally become part of the final composition after sintering. The lubricant liquefies under pressure and is generally removed thermally in the sintering process. This powder blend (mixture) is compacted into a shape by means of uniaxial, cold isostatic or other consolidation methods where the pressure applied causes the lubricant to liquefy and be uniformly distributed. The liquid phase forms over the surface of the solid phase particles. These liquid phase formers are uniformly distributed over the surface of the metallic particles by means of a lubricant that becomes liquid under applied pressure.

The liquid lubricant is not the liquid phase former. The liquid phase formers are other components which either separately or in combination with the metallic particle surface forms a liquid phase during sintering.

This process insures a uniform thin layer on the surface of the solid particles where the surface composition of the liquid phase forms and the solid particle contact complies with a phase diagram of these elements that possess a liquid phase when heated in the sintering operation. This allows a high degree of multiple contact liquid phase sintering. The liquid phase former which is a very fine synthetic graphite does not liquefy by itself, but only in contact with the solid particles that have solid solubility with each other.

This process of distributing the liquid phase former is infinitely more effective than having a heterogeneous distribution that does not produce the potential amount of sites to cause an effective coverage and composition for liquid phase development.

It has been found that through use of lubricants, such as APEX PS1000 b, which liquefy during compaction and are considered highly pressure sensitive that during compaction, the liquid lubricant disperses the fine liquid phase former uniformly over the surface of the particles whether the liquid phase former be synthetic graphite, boron, phosphorous or other liquid phase formers such as aluminum, copper, molybdenum, nickel, silicon, sulfur, zinc and their alloys.

The following examples of prior art techniques are provided for comparison purposes:

<u>Prior Art Example 1</u>

Typical manufacturing practice entails use of the prevalent method cited above in which Ancorsteel 85HP was blended with Southwestern Graphite grade 1651 in the amount of 0.65% although a range of 0.5-1.2% would be appropriate. Elemental nickel grade TD123 manufactured by Inco in an amount of 6.6% as well as a standard EBS lubricant in an amount of 1% were blended with the Ancorsteel 85HP and Southwestern

Graphite grade 1651 to obtain a homogenous blend. This powder mixture was subsequently uniaxially compacted in both mechanical and hydraulic presses at 50 tons per square inch obtaining a green density of 7.05 g/cc. The resulting green compacts were then sintered at 2050 degrees F in a nitrogen/hydrogen atmosphere for 45 minutes at temperature and obtained a sintered density of 7.15 g/cc to 7.20 g/cc (or 91.2 % to 91.8% of theoretical density.)

Prior Art Example 2

Alternately, Ancorsteel 85HP was blended with Southwestern Graphite grade 1651 in the amount of 0.65% although a range of 0.5-1.2% would be appropriate. 6.6% of elemental nickel grade TD123 manufactured by Inco and EBS in an amount of 1% were blended with the Ancorsteel 85HP and Southwestern Graphite grade 1651 to obtain a homogenous blend. This powder mixture was subsequently uniaxially compacted in both mechanical and hydraulic presses at 50 tons per square inch obtaining a green density of 7.05 g/cc. The resulting green compacts were sintered in a nitrogen/hydrogen atmosphere at a higher temperature for 2440F for 45 minutes at temperature and obtained a sintered density of 7.37 g/cc to 7.42 g/cc (or 94.0% to 94.6 % of theoretical density.)

In accordance with the invention, either iron powder, co-diffused or low alloy steel powders or combinations thereof were compacted so that the sintered part contained such elements as nickel, chromium, molybdenum, copper, low ash fine synthetic graphite and/or other alloying elements. The green compacts were sintered to a density of 7.84 g/cc or 100% of theoretical density.

By way of example, a powder metal, namely, Ancorsteel 85HP, was blended with APEX 1000b (as the lubricant) in the amount of 0.3% (although a range of 0.3-.5%

would be appropriate). Elemental nickel grade TD123 manufactured by Inco was blended in the amount of 6.6% of with the Ancorsteel 85HP and APEX grade 1000b to obtain a homogenous blend. Extra fine synthetic graphite grade Timcal KS6 at a 0.65% addition with a particle size distribution of d50 3.3 um and d90 of 6.5um was added (as the liquid phase former). This powder mixture was subsequently uniaxially compacted in both mechanical and hydraulic presses at 50 tons per square inch obtaining a green density of 7.15 g/cc.

The resulting green compacts were sintered simultaneously with the above cited composition at 2440 degrees F in a nitrogen/hydrogen atmosphere for 45 minutes at temperature to achieve a complex transient liquid phase sintering and obtained a sintered density of 7.84% (or 100% of theoretical density).

In addition to the Timcal KS6 synthetic graphite that was used, Timcal KS4 and F10 were also found to be suitable for the process. The following table indicates the particle sizes that were suitable:

Synthetic Graphite (Timcal)	typical particle size (microns)	maximum particle size (microns)
F10	5.8	12.0
KS6	3.3	6.5
KS4	2.4	4.7

In like manner, the following synthetic graphites from Asbury Carbon, Inc. were found to be suitable:

Synthetic Graphite (Asbury)	typical particle size (microns)
4827	2.0
4794	5.0
PM5 & PFSS	4.0 t 7.0
PI5	3.75 to 6.25
PFS8	6.0 to 11.0

The nickel that was used was obtained from INCO Special Products, INCO Limited of Wyckoff, New Jersey and the following were found suitable:

Fine Nickel Powder (INCO)	average particle size (microns)
123	1 to 2
255	2.2 to 2.8
287	2.6 to 3.3
110	0.8 to 1.5
210	0.5 to 1.0
210H	0.2 to 0.5

The invention thus provides a method of creating a powder metal master alloy or blend of metal powder with liquid phase formers which permit such powders to be pressed and sintered to close to full density.

Further, the invention provides the ability to produce a highly uniform green density compact with no density split because the liquid lubricant eliminates density splits.

Density splits are caused when die wall friction exists and as a result, when pressing from top to bottom, the densities facing the top and bottom punches are higher than in the center of the compact. In effect, an "hour glass" density profile occurs in the final product.

Elimination of density splits allows high precision and avoidable distortion when sintering to full density because non-uniform shrinkage of the part due to density variation is eliminated.

In the present invention, the lubricant liquefies upon compaction thereby coating the tooling in which the blended mass of material is being compacted thus giving a liquid film between the tool and the developing compact. This liquid between the tool and compact drives the friction force to zero thus eliminating density gradients within

the compact. With the compact having a uniform green density, upon sintering and consolidating to full density, the dimensions will remain uniform.